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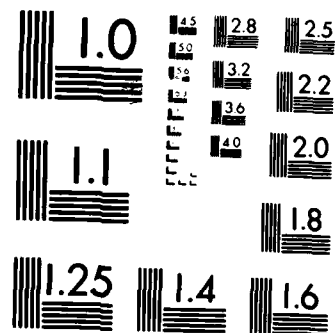
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NOTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for Public release. Distribution unlimited.	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) 16		7a. NAME OF MONITORING ORGANIZATION ONR	
6a. NAME OF PERFORMING ORGANIZATION Massachusetts Institute of Technology		7b. ADDRESS (City, State and ZIP Code) Department of Navy Arlington, Virginia 22217	
6b. ADDRESS (City, State and ZIP Code) Department of Chemistry 77 Massachusetts Avenue Cambridge, Massachusetts 02139		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION ONR		10. SOURCE OF FUNDING NOS. PROGRAM ELEMENT NO. N-00014-82-K PROJECT NO. NR631-618 TASK NO. 0322 WORK UNIT NO.	
8b. ADDRESS (City, State and ZIP Code) Department of Navy Arlington, Virginia 22217		11. TITLE (Include Security Classification) A Novel Polymeric Organosilazane Precursor to $\text{Si}_3\text{N}_4/\text{SiC}$ Ceramics.	
12. PERSONAL AUTHOR(S) Dietmar Seyferth and Gary H. Wiseman			
13a. TYPE OF REPORT Preprint		13b. TIME COVERED FROM _____ TO _____	
14. DATE OF REPORT (Yr., Mo., Day)		15. PAGE COUNT	
16. SUPPLEMENTARY NOTATION BOOK CHAPTER in "Ultrastructure Processing of Ceramics, Glasses, and Composites", (Vol.2)			
17. COSATI CODES FIELD GROUP SUB. GR.		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) silicon nitride, dichlorosilane, polysilazanes, ceramics.	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) The action of basic catalysts such as KH on the ammonolysis product of $\text{CH}_3\text{SiHCl}_2$, $[\text{CH}_3\text{SiH}_2\text{NH}]_x$, results in formation of polysilazanes of intermediate molecular weight (800-2000). Pyrolysis of these polysilazanes gives ceramic materials, which appear to be mixtures of Si_3N_4 , SiC and C, in yields of 80-85%. Preliminary experiments aimed at the preparation of ceramic bars, fibers and powder composites are described.			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT <input checked="" type="checkbox"/> DTIC USERS <input type="checkbox"/>			
21. ABSTRACT SECURITY CLASSIFICATION Unclassified		22a. NAME OF RESPONSIBLE INDIVIDUAL Kenneth J. Wynne	
22b. TELEPHONE NUMBER (Include Area Code) (202) 696-4410		22c. OFFICE SYMBOL NC	

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OFFICE OF NAVAL RESEARCH
CONTRACT NO0014-82-K-0322
Task No. NR 631-618

TECHNICAL REPORT NO. 16

A Novel Polymeric Organosilizane
Precursor to $\text{Si}_3\text{N}_4/\text{SiC}$ Ceramics

by

Dietmar Seyferth and Gary H. Wiseman

To be published in
"Ultrastructure Processing of
Ceramics, Glasses and Composites" (Vol. 2)

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February 6, 1985

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A Novel Polymeric Organosilazane Precursor to $\text{Si}_3\text{N}_4/\text{SiC}$ Ceramics.

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INTRODUCTION

Silicon nitride has become an important ceramic.¹ It has high thermal stability (to 1800°C), high oxidative stability (to 1500°C) and, if maximum theoretical density can be achieved, it is the hardest material which can be made at atmospheric pressure. Other advantageous properties of silicon nitride are its low electrical conductivity, low coefficient of thermal expansion, excellent thermal shock and creep resistance, high strength at elevated temperatures and corrosion resistance. Commercial interest in silicon nitride (and in silicon carbide) is high.

There are three major routes for the preparation of silicon nitride:

- 1) The high temperature reaction of gaseous nitrogen with elemental silicon ("nitridation").
- 2) The gas phase reaction of ammonia with a chlorosilane (SiCl_4 , HSiCl_3 , H_2SiCl_2) at higher temperatures.
- 3) The reaction of ammonia with SiCl_4 or HSiCl_3 in solution, followed by pyrolysis of the insoluble ammonolysis product after removal of ammonium chloride.

A newer method which we have investigated involves the reaction of ammonia with H_2SiCl_2 in an appropriate solvent to give a soluble silazane polymer which is then pyrolyzed in a nitrogen atmosphere to produce Si_3N_4 .² The initially formed polymer, however, is not stable at room temperature (under nitrogen). It undergoes a cross-linking reaction and within a few days sets to a clear, hard glass. Added to this drawback is the fact that the starting material, H_2SiCl_2 , is a rather hazardous chemical.³

The preceramic polymer route to silicon nitride nevertheless continued to be of interest and we have continued our research efforts in this area.

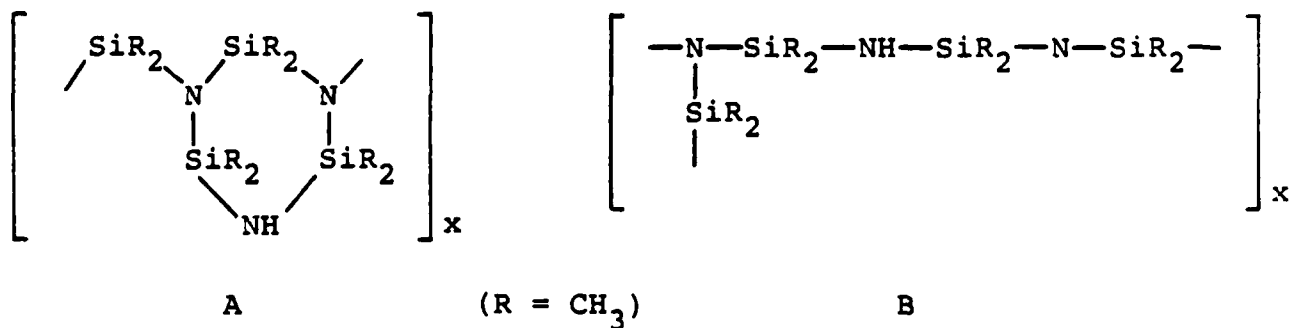
The room temperature cross-linking process which the initially formed H_2SiCl_2 ammonolysis product, $[\text{H}_2\text{SiNH}]_x$ cyclic and possibly linear oligomers, underwent must have involved chemistry of Si-H and N-H linkages, since cyclopolysilazanes of type $[\text{R}_2\text{SiNH}]_x$ (R = an organic group) are stable with respect to such cross-linking condensation reactions. The ideal preceramic polymer is one which will undergo a "self-curing" reaction (i.e., a cross-linking process) during the early or middle stages of its pyrolysis, so that a counterproductive decomposition to small (volatile) molecules is avoided and the yield of ceramic residue is maximized. This requires the presence of potentially reactive functionality in the polymer. In the case under discussion, the Si-H and N-H bonds are the reactive functionality. Unfortunately, this cross-linking process obviously was too facile, since it occurred even at room temperature. We reasoned that it was necessary to retain at least some Si-H bonds in the polymer for cross-linking purposes, but

that some of the Si-H groups in $[H_2SiNH]_x$ could be replaced by an organic group. This is, of course, a compromise. In order to obtain a more tractable preceramic system, a carbon-containing group is being added and it is probable that at least part of the carbon will end up in the ceramic product, as SiC or as free carbon. This is an acceptable compromise since silicon carbide also has very attractive properties. In order to minimize such introduction of carbon into the ceramic product, we used methyldichlorosilane, CH_3SiHCl_2 , in place of H_2SiCl_2 in our subsequent work.

Methyldichlorosilane is commercially available; it is a by-product of the "Direct Process", the high temperature, copper-catalyzed reaction of methyl chloride with elemental silicon and it is potentially inexpensive. In contrast to H_2SiCl_2 , it is a liquid under ambient conditions and it appears to be "safe". The ammonolysis of CH_3SiHCl_2 has been reported to give a mixture of cyclic and (possibly) linear oligomers, $[CH_3SiHNNH]_x$.⁴ We have examined this reaction in some detail. It is very easily effected by introducing gaseous ammonia into a stirred solution of CH_3SiHCl_2 in an appropriate anhydrous organic solvent (diethyl ether, tetrahydrofuran, benzene, etc.). The ammonolysis product, after removal of the precipitated NH_4Cl which also is produced, can be isolated as a clear, mobile liquid in high yield. Its C,H and N analysis and its spectroscopic (1H NMR, IR) data are in agreement with the $[CH_3SiHNNH]_x$ formulation. Molecular weight determinations (cryoscopy in benzene) of several preparations ranged from 280-320 g/mol ($\bar{x} = 4.7-5.4$). The product is quite stable at room temperature, but it is sensitive to moisture and must be protected from

the atmosphere. It is not stable to the conditions required for gas chromatographic analysis, but approximately one-half of it is volatile when heated to 100°C in high vacuum. This mixture of $[\text{CH}_3\text{SiHNNH}]_x$ oligomers is not suitable for ceramics preparation without further processing. On pyrolysis to 1000°C in a stream of nitrogen the ceramic yield is only 20%. Clearly, it is necessary to convert these cyclic $[\text{CH}_3\text{SiHNNH}]_x$ oligomers to material of higher molecular weight.

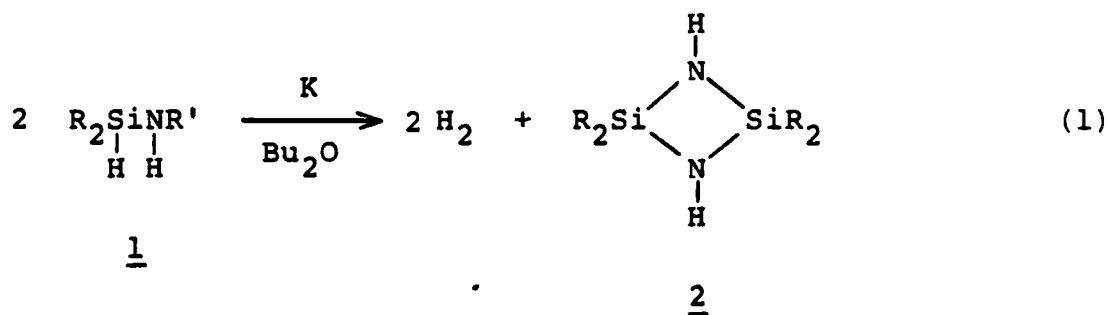
The conversion of the cyclopolysilazanes obtained by ammonolysis of diorganodichlorosilanes was investigated by Rochow and his coworkers some years ago when there was interest in polysilazanes as polymers in their own right.⁵ This procedure, the ammonium salt-induced polymerization, which in the case of hexamethylcyclotrisilazane appears to give polymers with units A and/or B, was applied in our investigations to the $\text{CH}_3\text{SiHCl}_2$ ammonolysis product. It produced a very viscous oil of higher



molecular weight, but the ceramic yield obtained on pyrolysis was a disappointing 36%. The $\text{Ru}_3(\text{CO})_{12}$ -catalyzed ring-opening polymerization of cyclo- $[(\text{CH}_3)_2\text{SiNH}]_4$, reported recently by Zoeckler and Laine,⁶ could not be adapted to the conversion of the $[\text{CH}_3\text{SiHNNH}]_x$

cyclics to a soluble polymer. An insoluble, rubbery solid was formed, which suggests that Si-H bonds as well as the Si-N bonds were activated by the transition metal catalyst.

The solution to our problem of converting the $[\text{CH}_3\text{SiH}_2\text{NH}]_x$ cyclics to a useful preceramic polymer was provided by earlier work of the Monsanto Company,⁷ who described the conversion of silylamines of type 1 to cyclodisilazanes, 2, in high yield by the action of potassium in di-n-butyl ether (eq.1). In this



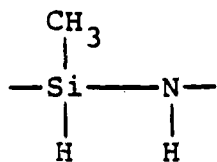
reaction, the potassium serves to metalate the NH functions to give 3. This then either eliminates H^- from silicon to give an



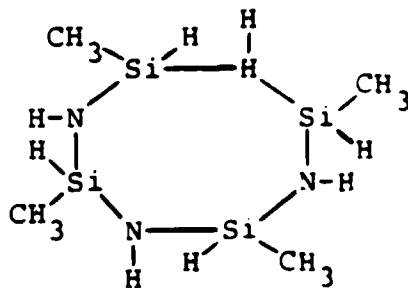
intermediate with a silicon-nitrogen double bond, $\text{R}_2\text{Si}=\text{NR}'$, which then undergoes head-to-tail dimerization to form 2, or alternatively, reacts with a molecule of $\text{R}_2\text{Si}(\text{H})\text{NHR}'$ to give intermediate 4

which undergoes cyclization to 2 with displacement of H^- . This interesting mechanistic question still needs to be resolved.

The repeating unit in the $[CH_3SiHNNH]_x$ cyclics is 5. Thus



5



6

the cyclic tetramer is the 8-membered ring compound 6. On the basis of equation 1, the adjacent NH and SiH groups provide the functionality which permits the molecular weight of the $[CH_3SiHNNH]_x$ cyclics to be increased.

Treatment of the CH_3SiHCl_2 ammonolysis product, cyclo- $[CH_3SiHNNH]_x$, with a catalytic amount of a base (generally an alkali metal base) strong enough to deprotonate the N-H function in a suitable solvent results in evolution of hydrogen. The resulting solution contains polymeric basic species and these are quenched by addition of methyl iodide or a monochlorosilane. After filtration to remove alkali metal halide, evaporation of the filtrate gives the product in essentially quantitative yield.

In our experiments we generally have used potassium hydride as the base, and the following is a typical experiment. The cyclo-silazane, $[CH_3SiHNNH]_x$ ($\bar{x} = 4.9$), 15.29 g (0.258 mol of $CH_3SiHNNH$ unit) was added under nitrogen to a slurry of 0.40 g (10 mmol,

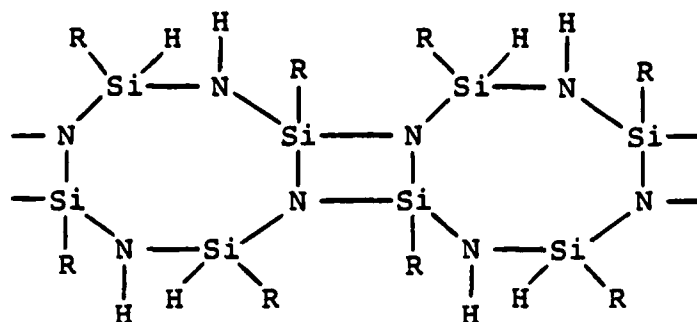
3.9 mol% based on the CH_3SiHNNH unit) of KH in 300 mL of tetrahydrofuran (THF). After gas evolution had ceased, 2.3 g of methyl iodide was added to quench all basic species, including basic sites on the resulting polymer. After the KI and solvent were removed by the appropriate workup, the product was isolated in the form of a white powder (in 99% yield) (average molecular weight, 1180) which was found to be soluble in hexane, benzene, diethyl ether, THF, and other common organic solvents.

For larger preparations it is of advantage to carry out the $\text{CH}_3\text{SiHCl}_2$ ammonolysis in the desired solvent, filter the ammonium chloride, and then to add the KH to the filtrate without isolating the $[\text{CH}_3\text{SiHNNH}]_x$.

Other bases (e.g., NaH, NaNH_2 , KOH, $\text{KB}(\text{sec-Bu}_3)\text{H}$, CH_3Li , etc.) may be used as catalysts. The reactions may be carried out in other ethers or in hydrocarbon solvents, and we have used reaction temperatures between 0°C and 65°C , but usually worked at room temperature. It is imperative to exclude atmospheric moisture since the $[\text{CH}_3\text{SiHNNH}]_x$ cyclics are readily hydrolyzed. The product polymer on the other hand, is of greatly diminished sensitivity to hydrolysis.

The composition of the polysilazane product of the experiment detailed above, ascertained by proton NMR spectroscopy, was $(\text{CH}_3\text{SiHNNH})_{0.39}(\text{CH}_3\text{SiHNNCH}_3)_{0.04}(\text{CH}_3\text{SiN})_{0.57}$ and its combustion analysis (C,H,N,Si) agreed with this formulation. These results are compatible with a process in which $(\text{CH}_3\text{SiHNNH})_n$ rings are linked together via Si_2N_2 bridges. Thus, if for example, the silazane 6 were to be polymerized in this way, the eight-membered rings could

be linked in a ladder polymer as shown in 7. The experimental



(R = CH₃)

7

(CH₃SiN)/(CH₃SiHNNH) ratio of ~1.3, however, indicates that further linking together of ladders via Si₂N₂ rings must have taken place. High polymers obviously are not formed, but the molecular weight is increased sufficiently so that pyrolysis proceeds satisfactorily.

A better understanding of the chemistry leading to these polysilazanes and of their structure is needed. For instance, in our various preparations the average molecular weights of the products obtained after the methyl iodide quench varied between 800 and 2000. Before the methyl iodide quench, silylamide functions (i.e., catalytically active functions) still were present, yet growth to higher molecular weights did not occur. Why is this so? The answer to this question must be connected with the solution structure and conformation of the polymers. If the polymerization involves linkage of the [CH₃SiHNNH]_x rings via Si₂N₂ rings in more than one direction, i.e., if it involves formation of linked ladders as postulated above, then a sheet structure will result.

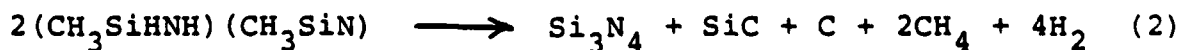
Sheet structures are common in silicon chemistry, for instance, in silicates, and in this connection some work reported by Kenney and his coworkers⁸ is of interest and possibly pertinent. In these studies, reaction of the silicate mineral chrysotile with hydrochloric acid and Me_3SiCl gave a stable polymer with a silicon-oxygen sheet framework. These polymer sheets curled up into scrolls when dry. It could be that if we have sheet polymers in our case, that in solution the repulsion of the negative charges of the amide functions will result in partial "curling up" of the sheets, thus introducing steric factors which would inhibit further growth. This, however, is speculation and future research will address the problem of the nature of the polymers in solution before and after the methyl iodide quench and of the solvent-free, solid polymer obtained in the preparations carried out in THF.

Whatever the structure of the silazane polymers obtained by KH treatment of the $[\text{CH}_3\text{SiHNNH}]_x$ cyclics, these polymers are excellent ceramic precursors. Examination of the polymers from various preparations by TGA showed the weight loss on pyrolysis to be only between 15 and 20%. The pyrolysis appears to take place in three steps: a 5% weight loss (involving evolution of H_2) from 100°C to 350°C; a 2% weight loss from 350-550°C and a 9% weight loss from 550°C to 900°C. During the 550-900°C stage a mixture of H_2 and methane was evolved. A trace of ammonia, in addition to H_2 , was lost between 350 and 550°C.

In a typical bulk pyrolysis experiment, a carbon sample boat containing the polysilazane from an experiment such as that described previously was placed (nitrogen atmosphere) in a mullite tube in a tube furnace. Pyrolysis was conducted under a slow

stream of nitrogen. The sample was heated quickly to 500°C and then slowly (over 8 h) to 1420°C and was held at 1420°C for 2 h. The ceramic powder was a single body and black. Powder X-ray diffraction ($\text{CuK}\alpha$ with Ni filter) showed only very small, broad peaks for $\alpha\text{-Si}_3\text{N}_4$. Scanning electron microscopy analysis showed little discernible microstructure with only a few very fine grains appearing at high magnification. The bulk appearance of the ceramic suggested that pyrolysis took place after the polymer had melted. There were many large holes and craters where the liquid bubbles apparently had burst. In such experiments ceramic yields usually were between 80 and 85%. The polymer used in the experiment above had been prepared in diethyl ether. It had a molecular weight of around 900 and went through a melt phase when it was heated. This could be shown when it was heated in a sealed capillary: it began to soften around 65°C, becoming more fluid with increasing temperature. The polymer prepared in THF is of higher molecular weight ($\overline{\text{MW}} = 1700\text{-}2000$) and does not soften when heated to 350°C. It gave an 83% yield of a black ceramic material on pyrolysis under nitrogen to 1000°C.

The pyrolysis of the silazane polymer may be represented by eq.2. Here the ceramic yield ($\text{Si}_3\text{N}_4 + \text{SiC} + \text{C}$) would be 83 wt%.



An analysis of such a ceramic product gave 12.87% C, 26.07% N, and 59.52% Si. By difference, % O would be 1.54%, but it is not necessarily present. This analysis is compatible with eq.2 and leads

to a ceramic constitution, based on the 4 Si of eq.2, of 0.88 Si_3N_4 , 1.27 SiC, 0.75 C, and (possibly) 0.09 SiO_2 .

Thus the chemistry leading to the desired ceramic product is quite satisfactory: the starting material is readily available, not expensive and safe to handle. Its reaction with ammonia is easily carried out and gives the cyclopolysilazane product in high yield. The conversion of the latter to the preceramic polymer is easily effected. It requires only a catalytic quantity of base and the polymer is easily isolated in essentially quantitative yield. The simple work-up (filtration, evaporation of solvents) allows the recovery and recycling of the anhydrous solvent. The polysilazane product is stable on storage at room temperature and is not especially sensitive to hydrolysis. Its pyrolysis gives a high yield of ceramic product and the volatiles evolved are not toxic or corrosive. It remains to be seen whether the ceramics applications are equally advantageous, but preliminary indications are promising.

Among potential applications of preceramic polymers which are of current interest are the following:

- 1) The forming of the polymer into complex shapes and its subsequent pyrolysis to give a ceramic material of the same shape (but not necessarily the same size).
- 2) The spinning of such polymers into continuous fibers whose subsequent pyrolysis would give ceramic fibers.
(Note the current importance of graphite fibers and the great interest in the Nicalon SiC fibers which were developed in Japan.)

- 3) The use of such polymers as matrix material for carbon or ceramic fibers, or as a binder for ceramic powders (with subsequent pyrolysis to form the ceramic).
- 4) The production of oxidation-resistant coatings on otherwise oxidizable materials (such as carbon-carbon composites). After the polymer coatings has been made, it would then be pyrolyzed to give the ceramic coating.
- 5) The infiltration of porous ceramic bodies such as ones obtained from reaction-sintered silicon nitride by the polymer itself (if liquid) or by a solution of the polymer, with subsequent pyrolysis to form the ceramic, resulting in better strength, oxidation resistance, etc., of the body.
- 6) The formation of thin films of the ceramic material for electronics applications.

Our initial research has dealt with the first three of these potential applications. In an investigation of the conversion of a shaped body of the polymer to a ceramic body we studied the pyrolysis of polysilazane bars. The problems associated with such a conversion have been pointed out by Rice.⁹ However, our ceramic yield is high and we could prepare a polysilazane which does not melt, so we were hopeful that this application would be successful. Bar-shaped bodies of the polysilazane prepared in THF solution were prepared by first uniaxially pressing a sample in a rectangular steel die and then isostatically pressing the resulting bar at 40,000 psi. Pyrolysis in a tube furnace under nitrogen (10°C per min to 1100°C)

gave a coherent, rectangular ceramic bar which had not cracked or bloated and could not be broken by hand. Even more promising were such preliminary experiments in which blends of the nonmelting and the meltable polysilazanes were used.

Fiber-reinforced composites as engineered structural materials are a very important area of research and development in current materials engineering¹⁰ and reviews which deal with the desired properties of ceramic fibers and composites have been published by Rice.¹¹ The Japanese Nicalon silicon carbide-containing fiber¹² has aroused much interest and also has prompted research to find other ceramic fibers, hopefully with better high temperature properties.

In collaboration with ceramists at the Celanese Research Company it was found that our meltable polysilazane cannot be melt-spun. Apparently, the thermal cross-linking process which is so effective in giving a high ceramic yield on pyrolysis takes place in the heated nozzle of the spinning machine and quickly gives infusible polymer. However, the infusible polysilazane which is obtained when the preparation is carried out in THF solution can be dry-spun. In this process the solid polysilazane is dissolved in an appropriate solvent and then is extruded through a spinneret into a heated drying chamber in which the solvent is volatilized, leaving the solid polymer. These polymer fibers could be pyrolyzed to give ceramic fibers. In simpler experiments, it was shown that fibers one to two feet in length could be drawn from the sticky, waxy solid which remained when a toluene solution of the polysilazane was evaporated.

Pyrolysis of these fibers under nitrogen produced long, flexible black fibers. This aspect of our work is in only at a very early stage, but these initial observations are encouraging.

We also have studied the possibility of preparing ceramic powder composites using our polysilazane as a binder. The preparation of such composites (using commercial samples of fine α -SiC, β -SiC and α -Si₃N₄ of 0.36-0.4 μ m mean particle size) required appropriate dispersion studies which cannot be described here. Best results were obtained using a blend of the meltable and the infusible powder. The ceramic powder was dispersed in a solution of toluene containing the appropriate weight of polysilazane and then the toluene was evaporated using a rotary evaporator, leaving a waxy residue. Vacuum distillation served to remove the remaining solvent to leave chunks of solid material. These were finely ground and pressed into a bar at 5000 psi. Isostatic pressing to 40,000 psi followed and then the bars were pyrolyzed in a tube furnace under nitrogen (10°C a minute, to 1100°C). The maximum density (\sim 2.4 g/cc) was achieved in these experiments with a polymer loading of 30%. However, all bars were relatively weak. SEM micrographs of the fracture surfaces of the bars showed that all of these composites had many large cracks throughout the bodies. These cracks probably resulted from nonuniform shrinkage.

In conclusion, we have shown in this work that polysilazanes prepared from the base-catalyzed polymerization of the cyclopoly-silazanes obtained in the ammonolysis of methyldichlorosilane are potentially useful for the fabrication of ceramics in

"unusual forms", especially as fibers. We also have demonstrated for the first time that monolithic ceramic bodies can be prepared by pyrolysis of the appropriately-shaped polymeric precursor. These polysilazanes also may prove to be useful as dispersants for SiC and Si₃N₄ powders. Composites can be prepared from these powders by using the polysilazanes as binders which themselves are converted to ceramic materials on pyrolysis. Further progress on these and other applications of our polysilazanes as "preceramic materials" will require close collaboration between the chemist and the ceramist since further "tailoring" of the chemistry probably will be needed to provide the systems which best meet the ceramic requirements.

A preliminary communication on this work has appeared¹³ and a patent has been issued.¹⁴

Acknowledgment. This work was supported in part by the Office of Naval Research.

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